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Application of the compatibility factor to the design of segmented and cascaded thermoelectric generators

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Using thermoelectric compatibility, efficient thermoelectric generators are rationally designed. With examples, compatible and incompatible systems are explained and materials proposed for targeted development. The compatibility factor explains why segmentation of $(AgSbTe_2)_{0.15}(GeTe)_{0.85}$ (TAGS) with SnTe or PbTe produces little extra power, while filled skutterudite increases the efficiency from 10.5% to 13.6%. High efficiency generators are designed with compatible *n*-type La_2Te_3, and similar *p*-type material, while incompatible SiGe alloys actually reduce the efficiency. A refractory metal with high *p*-type thermopower (>100 μV/K) is required for development. Cascaded generators avoid the compatibility problem. The thermoelectric potential provides a simple derivation of the cascading ratio.
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The efficiency of a thermoelectric generator is governed by the thermoelectric properties of the generator materials and the temperature drop across the generator. The temperature difference, ΔT, between the hot side (T_h) and the cold side (T_c) sets the upper limit of efficiency through the Carnot efficiency $\eta_c = \Delta T/T_h$. The thermoelectric material governs how close, the efficiency can be to Carnot primarily through the thermoelectric figure of merit, z, defined by $z = \alpha^2/\kappa\rho$. The relevant materials properties are the Seebeck coefficient α, the thermal conductivity κ, and electrical resistivity ρ, which all vary with temperature.

Thus, to achieve high efficiency, both large temperature differences and a high figure of merit materials are desired. Since the material thermoelectric properties (α, ρ, κ) vary with temperature, it is not desirable or even possible to use the same material throughout an entire, large temperature drop. Ideally, different materials can be *segmented* together (Fig. 1), in that a material with high efficiency at high temperature is segmented with a different material with high efficiency at low temperature. This way, both materials are operating only in their most efficient temperature range.

We have shown[1] that for the exact calculation of thermoelectric efficiency, the thermoelectric compatibility must also be considered. The maximum efficiency (determined by z) is only achieved[1] when the relative current density u (ratio of the electrical current density to the heat flux by conduction: $u = J/\kappa\nabla T$) is equal to the compatibility factor $s = (\sqrt{1+zT} - 1)/\alpha T$.

In an efficient generator the relative current density is roughly a constant throughout a segmented element (typically u changes by less than 20%). Thus, the goal is to select high figure of merit materials that have similar compatibility factors. If the compatibility factors differ by a factor of 2 or more, a given u cannot be suitable for both materials and segmentation will not be efficient. Compatibility is most important for segmented generators because the thermoelectric material properties may change dramatically from one segment to another. Other factors (not considered here) may also affect the selection. These include thermal and chemical stability, heat losses, coefficient of thermal expansion, processing requirements, availability and cost. For this analysis, we consider only the thermoelectric properties in the one-dimensional heat flow problem. The following examples demonstrate how the materials selection can be made rational by considering both z and s.

To provide quantitative results that are easy to compare, the single element (*n*- or *p*-type) efficiencies were calculated.[2] The overall efficiency is close to the average of the *n*- and *p*-type single element efficiencies. To calculate the variation of $u(T)$ with temperature, the differential equation

$$\frac{d(1/u)}{dT} = -\frac{1}{u^2}\frac{du}{dT} = -T\frac{d\alpha}{dT} - u\rho\kappa, \tag{1}$$

derived from the heat equation, must be solved. For computation, this can be approximated by combining the zero Thomson effect ($d\alpha/dT = 0$) solution with the zero resistance ($\rho\kappa = 0$) solution.

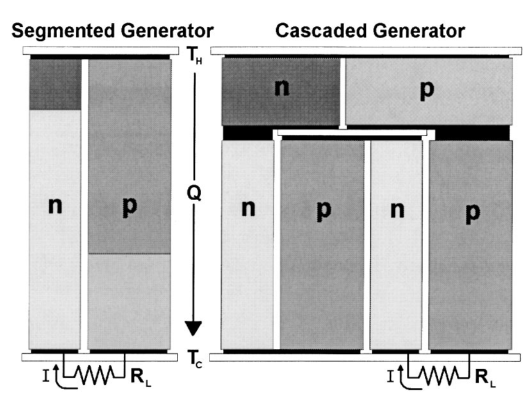

FIG. 1. Schematic diagram comparing segmented and cascaded thermoelectric generators.

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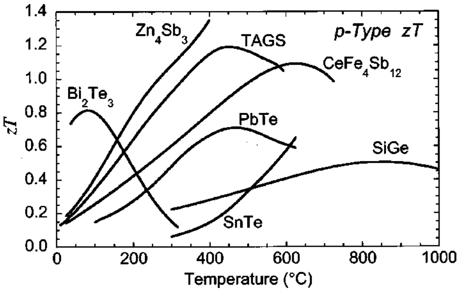

FIG. 2. Figure of merit (zT) for p-type materials.

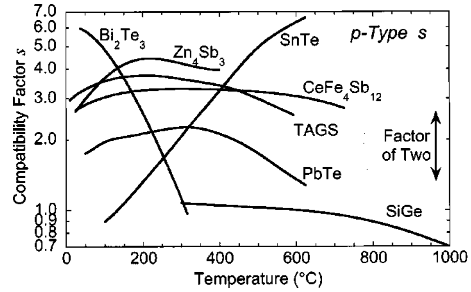

FIG. 3. Compatibility factor (s) for p-type materials.

$$\frac{1}{u_2}=\frac{1}{u_1}\sqrt{1-2u_1^2\overline{\rho\kappa}\Delta T}-\overline{T}\Delta\alpha, \tag{2}$$

where $\Delta\alpha=\alpha(T_2)-\alpha(T_1)$ and $\overline{\rho\kappa}$ denotes the average of $\rho\kappa$ between T_1 and T_2. Equation (2) is also valid to calculate the change in u at the interface between segmented materials where α is discontinuous ($\Delta T=0, \Delta\alpha\neq 0$).

Once $u(T)$ is known, the efficiency of a single thermoelectric element (n or p type) can be calculated from

$$\eta=1-\frac{\alpha_c T_c+1/u_c}{\alpha_h T_h+1/u_h}. \tag{3}$$

The subscripts h and c denote the value at the thermoelectric hot or cold side [T_h = hot side temperature, $\alpha_h=\alpha(T_h)$].

As the first example, consider the TAGS-SnTe segmented p-type thermoelectric generator element that has been used successfully on several NASA space missions.[3] The TAGS material [$(AgSbTe_2)_{0.15}(GeTe)_{0.85}$] must be maintained below 525 °C (or lower for long term applications), while the PbTe n-type element can operate to 600 °C. To achieve a 600 °C system, a segment of another p-type material is added to the TAGS p leg between 525 and 600 °C.

From zT (Fig. 2), it appears that p-type PbTe would be a better choice than SnTe for the 525–600 °C segment. However, the compatibility factor (Fig. 3) for p-PbTe drops much lower than that of TAGS, and segmentation actually results in a decrease in efficiency (Table I). SnTe has a closer compatibility factor to TAGS (higher is also beneficial), and thus produces a higher efficiency segmented generator, despite the lower zT, compared to PbTe. By alloying PbTe and SnTe, a more compatible material is produced with acceptable zT, and this is used in actual TAGS generators.

TABLE I. Maximum single element efficiencies for thermoelectric generators. $u(T_c)$ is the relative current density that gives the maximum efficiency.

Material	Efficiency (%)	T_c (°C)	$T_{\text{interface}}$ (°C)	T_h (°C)	$u(T_c)$ (V^{-1})
p-TAGS	10.45	100		525	2.97
p-TAGS/PbTe	10.33	100	525	600	2.33
p-TAGS/SnTe	11.09	100	525	600	2.84
p-TAGS/$CeFe_4Sb_{12}$	11.87	100	525	600	2.94
p-TAGS/$CeFe_4Sb_{12}$	13.56	100	525	700	2.88
p-SiGe	4.23	525		1000	0.85
p-TAGS/SiGe	9.89	100	525	1000	1.12
n-PbTe	9.87	100		600	−2.00
n-pbTe/$CoSb_3$	11.30	100	600	700	−1.97
n-PbTe/SiGe	13.76	100	600	1000	−1.46
n-PbTe/La_2Te_3	15.56	100	600	1000	−1.80
n-SiGe	5.44	600		1000	−1.29

A compatible and high efficiency material to segment with TAGS is p-type filled skutterudite such as $Ce_{0.85}Fe_{3.5}Co_{0.5}Sb_{12}$ ($CeFe_4Sb_{12}$ in Figs. 2 and 3). Filled skutterudite produces over twice the increase in efficiency (Table I) compared to SnTe.

Further increases in efficiency of PbTe/TAGS generators can be achieved by segmenting with both p- and n-type skutterudite ($CeFe_4Sb_{12}$ and $CoSb_3$) and increasing the hot side temperature (e.g., to 700 °C in Table I).

For the highest efficiency, it is necessary to use the highest temperature difference possible because of the Carnot factor. The thermoelectric hot side in a thermoelectric generator used for space applications can achieve 1000 °C. Many of the refractory materials with high zT, such as SiGe or boron carbide,[4] have low electrical conductivity with a high Seebeck coefficient, and therefore low compatibility factors (SiGe, Figs. 2–5). The low compatibility factors reduce their suitability for segmentation with PbTe, TAGS, or skutterudite materials. p-type SiGe is so incompatible, that a decrease in efficiency would actually occur (Table I).

Rare earth chalcogenides,[4] particularly La_2Te_3,[5] not only have high zT, but also have higher s compatible with PbTe and skutterudite thermoelectric materials. Segmenting PbTe with La_2Te_3 results in an increase in efficiency from 9.9% to 15.6%.

For the high temperature p-type element, a high zT material that is also compatible with PbTe, TAGS, or skutterudite has not been identified. To utilize La_2Te_3 in the n element, some high temperature p-type material must be used. Even if the material has low $zT\approx 0.5$, it will produce some power, *as long as it is compatible*. For a material with a low zT to be compatible with PbTe, TAGS, or skutterudite it must have $s>1.5\ V^{-1}$, ideally $s\approx 3\ V^{-1}$. Since $s\approx z/2\alpha$, the $zT\approx 0.5$ material cannot be a high Seebeck coefficient band or polaron semiconductor.

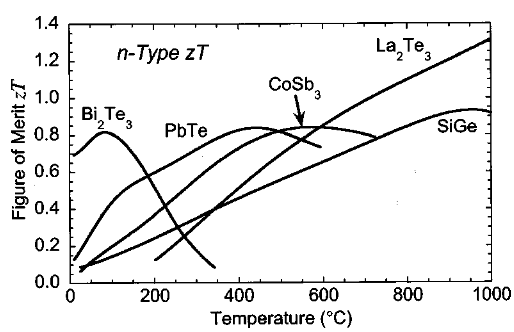

FIG. 4. Figure of merit (zT) for n-type materials.

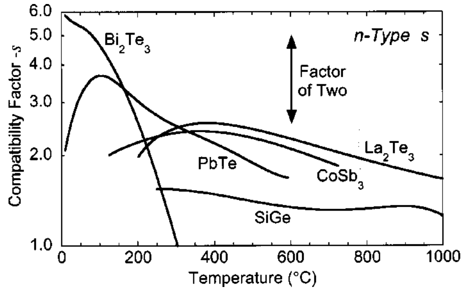

FIG. 5. Compatibility factor (s) for n-type materials (negative).

Materials with high z and s have thermoelectric properties typical of high α metals. In a metal, the thermal conductivity is dominated by the electronic contribution given by the Wiedemann-Franz law $\kappa_e = LT/\rho$, where $L \approx 2.4 \times 10^{-8}\ \mathrm{V}^2/\mathrm{K}^2$. The compatibility factor $s \approx \alpha/(2\kappa\rho) \approx \alpha/(2LT)$ would then be appropriate if α is greater than 100 μV/K at 1000 K.

Thus, the material that is most necessary for the development of high efficiency thermoelectric generators is a refractory p-type metal with a reasonably high Seebeck coefficient, much like a p-type version of La_2Te_3, which has α and ρ increasing linearly with T.

The compatibility issue can be avoided by cascading (instead of segmenting) a thermoelectric generator. In a cascaded system (Fig. 1) there are, in principle, independent electrical circuits for each stage, allowing for independent values of u. In this way, different, optimal values of u can be used for each stage.

In practice, it is best not to connect the high temperature stages directly to the load. Such connectors would be inefficient, because if they have low electrical resistance they will conduct heat away from the hot side (due to Wiedemann-Franz law); if they have high electrical resistance, there will be additional Joule losses. To avoid such losses, the electrical current should pass from the high temperature stage to the load by going through the thermoelectric elements of the low temperature stage (Fig. 1).

The differing values of u are provided by having a different number of couples in each stage. The ratio of the number of couples (N_2/N_1) in the cooler stage (Stage 2, N_2 couples) to that of the hotter stage (Stage 1, N_1 couples), here called the *cascading ratio*,[6] is derived by equating the heat out of the hot stage to the heat input to the cold stage. Thus, T in the following formulas is the interface temperature between the two stages. This can be expressed succinctly by using the thermoelectric potential $\Phi = \alpha T + 1/u$ (Ref. 1). The rate of heat entering or existing a thermoelectric couple is simply the current I times the sum of the thermoelectric potential for the n and p elements:

$$Q_{\mathrm{couple}} = I\Phi_{\mathrm{couple}} = I\left(\alpha_p T + \frac{1}{u_p} - \alpha_n T - \frac{1}{u_n}\right), \tag{4}$$

which includes the Peltier and conduction heat terms (the Peltier contribution is missing in Ref. 7).

For maximum efficiency, u will be approximately equal to s. Equating the heat from N_1 stage 1 couples with N_2 stage 2 couples, operating with the same electrical current I, gives:

$$\frac{N_2}{N_1} = \frac{\Phi_1}{\Phi_2} \approx \frac{\alpha_{1,p}T + \dfrac{1}{s_{1,p}} - \alpha_{1,n}T - \dfrac{1}{s_{1,n}}}{\alpha_{2,p}T + \dfrac{1}{s_{2,p}} - \alpha_{2,n}T - \dfrac{1}{s_{2,n}}}. \tag{5}$$

The approximation where the thermoelectric properties (α, ρ, κ) are constant with respect to temperature is given by Harman.[6] For SiGe cascaded with TAGS/PbTe, the optimum cascading ratio is 2.21, so that there should be about twice as many TAGS/PbTe couples as SiGe couples. With this cascading ratio, the efficiency of the generator can achieve the sum of the two stages, $10.39\% + 4.39\% = 14.78\%$ (the maximum efficiency of a stage is approximately the average of the n- and p-type element).[2]

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